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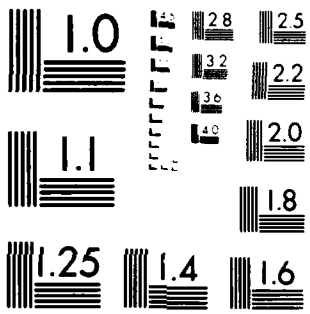

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POLLUTION ABATEMENT: A METAL RECOVERY TECHNIQUE FOR TREATING ELECTROPLATING EFFLUENTS

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An investigation was conducted into the state-of-the-art of existing and emerging techniques and systems for treating electroplating effluents. No laboratory evaluations were attempted. Ten techniques were studied to determine if they would (1) clean the effluents by returning pure water to the rinse system of the plating operation, (2) recover the plating metals and (3) meet a zero discharge requirement of the Environmental Protection Agency. Three of the methods studied were found to meet these requirements. One

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method has been recommended for use after a complete field evaluation.

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INTRODUCTION

Electroplating processes at the Naval Air Rework Facilities (NARFs) produce the highest toxicity and largest volume of effluent of all operations performed by these activities. The toxicity of this effluent is due primarily to the heavy metals used in the plating operation, such as hexavalent chromium, nickel and silver as well as other toxic materials such as cyanides. The high volume of effluent is due to the large quantities of water that are used during rinsing cycles. Currently, this effluent is sent to sanitation systems, which are inadequate for handling heavy metals and which lack the techniques for the destruction of toxic chemicals to meet a zero discharge requirement. Therefore, pollutive effluents are being discharged into waterways and other disposal sites.

In an attempt to meet the zero discharge requirement which has been established by the Environmental Protection Agency (EPA), a study was conducted of methods for controlling electroplating effluent discharge. This work was accomplished under the reference (a) work request and as planned under reference (b).

APPROACH

An investigation was conducted of the state of the art of existing and emerging techniques for treatment of electroplating effluents. This investigation was limited to a literature survey of methods and procedures for treating electroplating waste water before discharge. No laboratory evaluations were performed on any of the techniques.

The following treatment techniques listed in reference (c) were evaluated: (1) hydroxide precipitation; (2) sulfide precipitation; (3) evaporation; (4) reverse osmosis (RO); (5) electrodialysis; (6) Donnan dialysis; (7) electrolytic technique; (8) insoluble starch xanthate (ISX); (9) activated carbon and (10) solvent based systems. Each of these methods was evaluated based on potential integration into NARF electroplating operations, advantages and disadvantages and the ability to meet the zero discharge requirement without auxiliary equipment.

DISCUSSION OF TECHNIQUES

BACKGROUND

Treatment of electroplating effluent at the NARFs under the present system is very difficult and nearly impractical to accomplish, in order to meet the zero discharge requirement. Treatment is currently done at the end of the line at the sanitation treatment. Large volumes of water are processed which contain small quantities of pollutive materials as compared to the volume of water; yet these chemicals must be removed or destroyed before this water is discharged. The cost of the chemicals to treat this volume of polluted water is extremely high. Under this investigation, the concept of treating/controlling the effluent at the source, the plating process, is being investigated.

A two pronged approach was devised to accomplish control of the effluent in the plating process; (1) material substitution and (2) treatment of the effluent at the source by a recovery method. Under previous NAVAIRDEVCEN efforts, two material substitution programs were initiated, (1) substitution of trivalent chromium for hexavalent chromium and (2) a non-cyanide cadmium plating bath for a cyanide cadmium bath. Effort on the chromium substitution concept was terminated based on information from the NARFs that indicated the trivalent chromium would not meet the needed physical plating properties that the hexavalent chromium provided. On the non-cyanide cadmium system (Kadizid), preliminary results indicated that it was less than satisfactory (reference (d)). It appears that for this system, the item to be plated must be perfectly clean before the plating metal will adhere to the surface.

In conjunction with the effluent recovery method, an effort is underway to investigate methods and techniques to treat the electroplating effluent at the source. A short bed, rapid recycle ion exchange system has been procured and evaluated in an operational chromium plating line at the NARF, Jacksonville, Florida. This unit is designed to recover plating metals and return purified water to the rinse system of the plating line. The results of the evaluation, reference (e), indicated that the system did perform satisfactorily and recommended its use in treating chromium electroplating effluent.

TECHNIQUES

Under this study, other techniques are being investigated as alternative methods for treatment of electroplating effluent, to enable flexibility, efficiency of operation and possible cost savings. The techniques are:

Hydroxide Precipitation

This system is one of a number of conventional systems used to treat electroplating effluent. This technique is based on chemical reactions which remove pollutants by changing their chemical properties, and reducing their solubility and/or toxicity. Cyanide removal is accomplished with alkaline chloride, and the reduction of hexavalent chromium is best accomplished by the use of sulfur dioxide. The removal of dissolved metals from the effluent is accomplished by adjusting the pH of the effluent to form carbonates or hydroxides which can be readily removed as sludge. This technique can be integrated into the rinsing cycle to abate pollution. The disadvantages of this technique are the generation of large quantities of sludge that must be disposed of, the loss of expensive plating chemicals and, because it is only 90% efficient it does not meet the zero discharge requirement.

Evaporation

The evaporation technique is a reliable technique which also produces high quality water. It is a system that is utilized because a

real savings can be realized in the recovery of chemicals and water. It can be used in any metal finishing line for recovery purposes. The disadvantages are its high energy requirement to remove the water by evaporation with the resultant high concentration of impurities, plating metals and other elements. To reduce the concentration of metals and impurities, auxiliary equipment such as an ion exchange system is required, increasing the total cost of the system. Another disadvantage is the evaporators themselves must be constructed from a material that will withstand the corrosive nature of the effluent to which it will be exposed. This would require a separate evaporator for each plating line.

Membrane Techniques

There are three specific techniques using membranes as a means of treatment and recovery; reverse osmosis, electrodialysis and Donnan dialysis. There are advantages applicable to all three methods, low capital cost, low space requirements, low labor cost, low energy use and they produce no sludge. There are disadvantages associated with each technique. These will be discussed under each technique.

a. Reverse osmosis is a pressure driven membrane separation process in which a feed stream under pressure is separated into a purified permeate stream and a concentrate stream by selective permeation of water through a semi-permeable membrane. Reverse osmosis is incapable of achieving very high concentration because the operating pressure does not, in most cases, exceed the osmotic pressure of the solution. Therefore, a finite division between the purified permeate and the concentrate does not occur. Certain small non-ionized molecules are not completely rejected by the membrane and thus contaminate the permeate stream. Membrane performance generally degrades with time, requiring periodic replacement. Also, the presence of oxidizing substances, such as chlorine and chromic acid tend to destroy commercial membranes.

b. Electrodialysis is a membrane technique where separation is accomplished by selectively transporting ions through membranes under the influence of an electrical potential applied across the membrane. By imposing an electrical potential across a cell, in which the ions are bounded on one side by a membrane permeable only to cations and on the other side by another membrane permeable only to anions, plating waste water can be made to separate into a cation rich waste water and a anion rich waste water. By passing the same waste water sequentially past both permeable membranes while the electrical current is applied, the contaminants can be concentrated in one stream while the waste water is freed of pollutants.

This technique is suitable for recovery of ionized particles such as metal salts, cyanides or chromates from metal finishing effluents. It achieves high concentrations, so recovered plating chemicals can be returned directly to the plating bath.

The disadvantages of this technique are, it is not economical for treatment of very dilute effluents nor can it produce effluent to meet the zero discharge requirement.

c. Donnar dialysis is a membrane technique based on the known Donnan exclusion principle, which is a steady state ion exchange. In Donnan dialysis, the driving force is a difference in concentration across the membrane and does not require external, electrical or other forms of energy. The technique involves passing the effluent containing metal ions through the inside of small diameter tubes fabricated from a cation exchange membrane. A suitable regenerant (H_2SO_4) is passed over the outside of the tubes countercurrent to the effluent flow. The metal ions can be easily concentrated to over ten times the original concentration of the effluent stream. This technique is capable of concentrating metals from dilute effluents and can easily achieve less than 1 ppm levels of metal in the regenerant solution. Donnan dialysis concentrates only cations and does not concentrate other constituents of the effluent.

The disadvantages of Donnan dialysis is that acidified water is produced rather than pure water. The problem of acidic water is more pronounced if this techique is used on more concentrated effluent streams such as the first rinse tank after plating. This acidic water must be neutralized before it can be used in the rinse system or discharged.

Electrolytic Techniques

These techniques are considered effective in plating out metals, oxidizing cyanide or reducing chromium from plating effluents. Electricity is the only operating cost and no chemicals are needed. However, for dilute effluents, such as less than 100 ppm, the electrical resistance of effluents is high and the cost of electricity becomes prohibitive. The EPA has participated over the years in the development and demonstration of several electrolytic methods all of which use some means to reduce the electrical resistance of the cell.

A pilot plant electrolytic system was designed to concurrently remove metals and oxidize cyanide. The system employs an electrolytic cell with a cathode bed composed of thin particles, a graphite particle bed anode and a cellphane separator. Low voltage direct current is applied. The best removals are obtained with sodium chloride (NaCl) added as a supporting electrolyte and with recirculation of the anode bed effluent. No attempt is made to recover metals, but 78-84% removal of cyanide, 95% removal of cadmium and 57% of zinc were achieved. Thus, the treated waste water could be reused in the plant. This system is not yet available commercially.

Insoluble Starch Xanthate

This is a new low cost technique using insoluble sodium starch as the removal medium. This technique removes heavy metals from waste water to a friction of a ppm. It is also effective for instantaneous removal of all metals, including hexavalent chromium and complexed metals from concentrated and dilute solutions. The removal of hexavalent chromium with insoluble starch xanthate requires lowering the ph to below 3 with subsequent raising the ph to above 7. The chromium

is removed as trivalent chromium starch xanthate or chromic hydroxide.

The disadvantage of this technique is that it generates a large quantity of sludge which must be disposed. It requires ten pounds of ISX to remove one pound of copper and three pounds of ISX to remove one pound of gold. There is no data on the amount of ISX required to remove chrome nickel or cadmium. At present, this technique is only being used to recover gold.

Sulfide Precipitation

This technique is an effective process for the treatment of industrial waste containing highly toxic heavy metals such as produced at the NARFs. The attractive features (reference (f)) of this technique are: (1) it attains a high degree of metal removal over a wide pH range; (2) effective precipitation of certain metals such as As, Cu, Cd and Hg even at low pH; (3) short retention time in the reaction tank because of high reactivity of the sulfides and (4) the feasibility of selective metal recovery. With sulfide precipitation, the high reactivity of sulfides with heavy metal ions and the very low solubility of heavy metal sulfides over a wide pH range are significant advantages when compared to hydroxide precipitation techniques. Hydroxide precipitation of heavy metals followed by settling of the precipitates is most often used to treat industrial waste waters. However, the minimum solubilities for different metals occur at different pH values. Therefore, because the hydroxide precipitates are amphoteric, removal of minimum mixed metals cannot be achieved at a single pH value.

The sulfide precipitation technique appears to be an effective process for removing heavy metals, and it is gaining considerable acceptance in cleaning effluents before disposal. Most heavy metal sulfides have very low solubilities even at acidic pH values. As_2S_3, CuS, CdS and PbS can be completely precipitated even at pH=2, although ZnS precipitation would be incomplete at pH <4. The extent of metal sulfides precipitation is a function of pH, type of metal sulfide dosage and ions that might be present. There is some concern over safe disposal of sulfide sludges since they may be reoxidized and solubilized.

RESULTS OF INVESTIGATION

Results of this investigation indicate that of the ten effluent recovery techniques or systems studied, only three can meet the zero discharge requirements and at the same time recover plating metals from operational electroplating systems. These techniques are: (1) evaporation, (2) insoluble starch xanthate and (3) sulfide precipitation. Although these three techniques will accomplish the desired functions, there are disadvantages of each that must be considered before a selection is made. The evaporation techniques has a high energy requirement for evaporation and concentration of impurities. It also needs an ion exchange column or an activated carbon filter to overcome the concentrated impurities. Insoluble starch xanthate produces a very large quantity of sludge becau e it requi es ten pounds of starch to recover

one pound of plating metal. For the sulfide precipitation technique, it is suspected that the sulfide sludge may be reoxidized and solubilized.

Four of the techniques could not meet the zero discharge requirement. Of the other three remaining techniques, the electrolyte method is not commercially available, and limited data for activated carbon and solvent based systems precluded considering them for use as recovery systems.

CONCLUSIONS

It is therefore concluded that three techniques studied may have application in abating pollution by cleaning the electroplating effluent. Of these three techniques, the sulfide precipitation appears to be the most appropriate for NARF application. Energy consumption is non-existent, it does not produce large quantities of sludge and does not require auxiliary equipment.

RECOMMENDATIONS

It is recommended that the sulfide precipitation technique be considered for use to clean the effluent from electroplating operation at the NARFs and also for recovery of plating metals. It is further recommended that a field evaluation similar to that conducted for the short bed rapid recycle ion exchange system (reference (d)) be conducted to determine; (1) if the technique will recover hexavalent chromium, nickel, cadmium, (2) to what extent (quantity) recovery is possible, and (3) if the sludge produced is soluble or re-oxidizable.

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